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## **Chapter 3**

### **Refractory Materials and Coating Formation**



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## **1. REFRACTORY MATERIALS AND THEIR PROPERTIES**

### **1.1 General Introduction**

The refractory lining of a modern, high performance Portland cement kiln is a complex system performing different specific functions at various locations. These include:

- ◆ protection of the kiln shell and tyres from reaching excessive temperatures
- ◆ protection of the kiln shell against chemical attack by aggressive gases and liquids
- ◆ protection of the kiln shell from mechanical abrasion by kiln charge
- ◆ reduction of heat losses to acceptably low values
- ◆ increase of heat exchange between gases and kiln charge
- ◆ control of material flow

Whereas in the rotary kilns in service until the late 1930's these duties were performed by fireclay products of approximately 40%  $\text{Al}_2\text{O}_3$  content, the high performance kilns of today necessitate the use of a wide spectrum of specially developed high  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  refractory types. Within each of these main categories, each manufacturer has designed his product differently to incorporate the required degree of resistance to the combined chemical, thermal and mechanical attack that will be encountered in service.

From the viewpoint of clinker production, the financial outlay of relining a kiln (including removal and installation of the worn and new refractories) represents approximately 2-4 % of total cement manufacturing costs. The effective loss of cement sales resulting from reduced kiln availability constitutes, however, a much higher loss should the kiln be shut down for more than 10-15 days.

Within the plants of "Holderbank" Group, an estimated 30'000 tons of refractories are consumed each year which, when the following sales costs are assumed

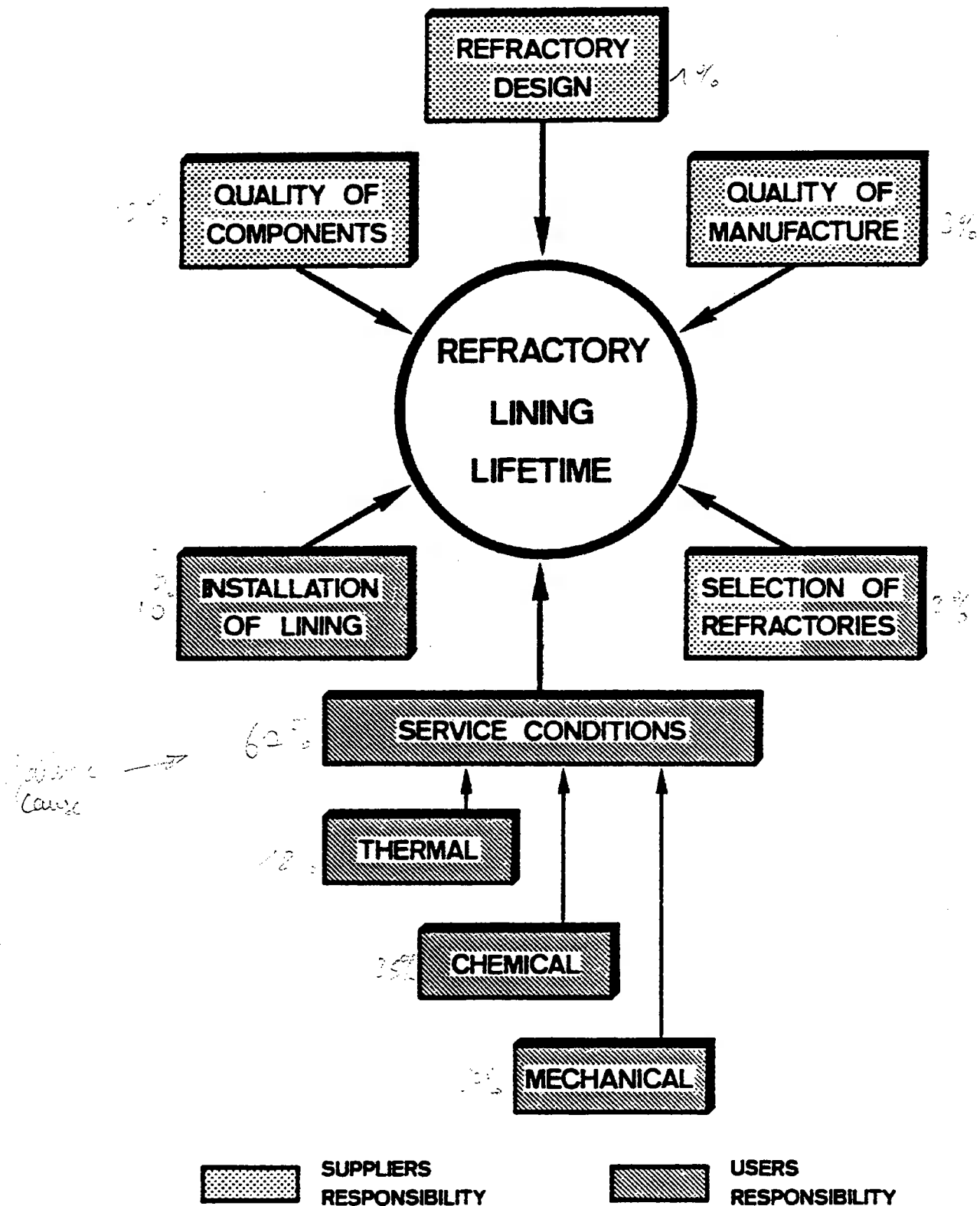
magnesite :	1'400 DM/ton
dolomite :	1'100 DM/ton
others :	1'050 DM/ton

results in an annual expenditure for refractory materials alone of \$20'000'000. To this already substantial sum must further be added the man-hours associated with relining, and lost cement sales resulting from 44'000 hr. of kiln down time.

It is therefore obvious that the life expectancy of the kiln refractory lining is a topic of basic financial importance. Depending on kiln zone, refractory types and production conditions, service lives in the critical sintering and transition zones may range from only several weeks to well in excess of 1 year.

The principal factors determining a linings service life are schematically displayed in Fig. 1, indicating those topics which lie within the responsibility of the refractory supplier and those over which the cement producer has most influence.

Fig.1 Factors Influencing Refractory Lining Lifetime



The recent reintroduction of coal-firing, together with the use of dry process kilns has resulted in refractories being subjected to appreciably increased attack by fused coal ash, by local reducing atmospheres and by alkali sulfates. To combat these trends, refractory manufacturers have recently increased their range of cement kiln refractories to include iron and chrome free periclase-spinel and magnesium silicate (forsterite) types.

The technological complexity of the kiln linings has been developed to such a stage and is of such financial importance that each plant should have a refractories specialist possessing a good basic technical/theoretical knowledge and having additionally sound practical experience. To help achieve this aim, the "Holderbank" Refractories Handbook for the Cement Industry is intended as a compact source of cement industry specific information and is intended for both newcomer and refractories specialist alike.

## **1.2 Classification of Refractory Products**

### **1.2.1 General**

Refractory materials are mainly composed of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Cr}_2\text{O}_3$  existing as the free oxide or combined together. They are defined according to ISO Standard R 836 as "non metallic materials or products having a minimum pyrometric cone equivalent of  $1500^\circ\text{C}$ . Internationally they are classified, according to PRE recommendations, as comprising of the following technological categories:

- ◆ dense, shaped refractory products .
- ◆ shaped insulating refractory products .
- ◆ prepared unshaped dense and insulating refractory materials

### **1.2.2 Chemical Classifications**

The different groups of refractory materials, based on their chemical composition, is listed in Table 1.

**Table 1** Chemical classification of dense shaped refractory products according to ISO 1109 1975 (E)

Designation		Quality Limits
Acid Group	High-alumina products Group 1	$Al_2O_3 \geq 56 \%$
	High-alumina products Group 2	$45 \% \leq Al_2O_3 < 56 \%$
	Fire-clay products	$30 \% \leq Al_2O_3 < 45 \%$
	Low-alumina fire-clay products	$10 \% \leq Al_2O_3 < 30 \%$ $SiO_2 \geq 85 \%$
	Siliceous products	$85 \% \leq SiO_2 < 93 \%$
	Silica products	$SiO_2 \geq 93 \%$
Basic Group	Basic products	
	- Magnesite	$MgO \geq 80 \%$
	- Magnesite-Chrome	$55 \% \leq MgO < 80 \%$
	- Chrome-Magnesite	$25 \% \leq MgO < 55 \%$
	- Chromite	$Cr_2O_3 \geq 25 \%$ $MgO \geq 25 \%$
	- Forsterite - Dolomite	$MgO, SiO_2$ $CaO, MgO$
Special Products	Special products on the basis of:	
	<ul style="list-style-type: none"> <li>- Carbon</li> <li>- Graphite</li> <li>- Zirconium silicate</li> <li>- Zirconium dioxide</li> <li>- Silicon carbide</li> <li>- Carbides (except silicon carbide)</li> <li>- Nitrides</li> <li>- Borides</li> <li>- Spinel (except chromite)</li> </ul>	
	Products based on more than one oxide (except basic prod.)	
	Products based on pure oxides, e.g. alumina, silica, magnesia, zirconium dioxide	
	High purity products	

As can be observed according to ISO Recommendations, there are

- ♦ acidic refractory products
- ♦ basic refractory products
- ♦ special products

each with a defined percentage of the component oxides in the finished products. In a further subdivision of the fireclay products (i.e. 30%  $Al_2O_3 < 45\%$ ), the following categories are recognized according to PRE/R 29:

**Table 2 Groups of Fireclay Products**

Group	$Al_2O_3$ content (%)
30	30-33
33	33-37
37	37-40
40	40-42
42	42-45

The properties of several ranges of refractories are provided in Table 3.

**Table 3 Composition and Properties of Refractory materials**

Refractory Materials	Alumina-rich refractories			Magnesite $MgO \geq 80\%$			Magnesite Chromite $55 \leq MgO \leq 80$	Chromite-magnesite $25 \leq MgO \leq 55$	Forsterite	Dolomite	Special basic products
				low in Fe	Fe-rich	Bricks					
$Al_2O_3$	45 - 50	60 - 72	80	$\leq 1$	$\leq 2$	$\leq 8$	4 - 11	$\leq 22$	1 - 10	0.8 - 1.1	3.2 - 4.3
$SiO_2$	45			0.8 - 3.5	$\leq 2.5$	$\leq 2.5$	1 - 3.5	$\leq 6$	35 - 40	0.7 - 1	7.1 - 9
$Fe_2O_3$	1 - 2	1 - 2		0.6 - 2.3	3.5 - 10	$\leq 12$	5 - 12	7 - 15	5 - 12	1	6.5 - 8
$MgO$	0.2	0.2		92 - 96	$\geq 80$	77 - 92	55 - 80	25 - 55	45 - 60	37	53 - 63
$CaO$	0.2	0.2		0.8 - 3.0	$\leq 4$	$\leq 3$	1 - 3	$\leq 2.5$	0.2 - 1.5	60	13.8 - 18.3
$Cr_2O_3$	-			$\leq 1$	$\leq 1$	$\leq 0.5$	6 - 20	15 - 35	1.5 - 10		6.4 - 8.2
$Na_2O + K_2O$		0.5 - 1.5									
Porosity %	19 - 22		20 - 25	16 - 22	18 - 24	16 - 25	16 - 23	17 - 24	16 - 23	16 - 22	20 - 24
Refractoriness under load $t_a$ °C (DfB)	1480 - 1550	1500 - 1650		1550 - $\geq 1700$			1550 - 1650		1600 - 1650	1550 - 1760	
Thermal conductivity at 1000°C Kcal/m °C h	1.2 - 1.5	1.5 - 2.2	1.5 - 2.2	2.5 - 3.5	2.5 - 3.5	1.8 - 2.6	2 - 3	1.5 - 2.5	1.6 - 2	2.3	2.9
Application in Transition zone	X	X	X		X		X	X		X	X
Application in Sinter zone			X	X	X	X	X	X	X	X	X
Predominant mineral phases	Corundum Mullite			Periclase Spinel Monticellite Mg-Ferrite Merwinite			Periclase Monticellite Forsterite Magnesioferrite Spinel Chromite Merwinite	Forsterite Periclase Magnesioferrite Spinel	CaO Periclase		



Appendix 1 Structures of "Spinel" Bricks

	Sinter type							
	Synthetic	Natural						
Pre-formed spinel grain								
Spinel formed during brick firing (ex. alumina grains)								
Spinel formed during brick firing (ex. alumina powder)								
Spinel formed during brick firing (mixed spinel types)								
<p>Spinel <math>\text{MgO} \cdot \text{Al}_2\text{O}_3</math>      <math>\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgO} \cdot \text{Al}_2\text{O}_3</math></p> <table><tr><td>Legend :</td><td>Scale : 200 <math>\mu\text{m}</math></td></tr><tr><td>Sinter <math>\text{MgO} \cdot \text{CaO}</math></td><td></td></tr><tr><td>Spinel</td><td></td></tr></table>			Legend :	Scale : 200 $\mu\text{m}$	Sinter $\text{MgO} \cdot \text{CaO}$		Spinel	
Legend :	Scale : 200 $\mu\text{m}$							
Sinter $\text{MgO} \cdot \text{CaO}$								
Spinel								

### 1.2.3 Nomenclature of Manufacturing Process

To provide further information on the various chemically based classes of shaped refractories, the manufacturer may supply additional characterizing information such as:

- ◆ process of shaping
- ◆ method of bonding the material

With regard to the shaping process, various methods are employed by the refractory industry in the manufacture of bricks.

Besides the casting of melts of specific compositions (fusion cast products), the methods of fine ceramics, such as slip casting, continuous extrusion or pressing of finely crushed materials, have been used increasingly during recent years.

However, the so-called coarse ceramic method is preferred for the manufacture of refractory bricks. Production by this technique includes the following steps:

- ◆ crushing
- ◆ classification (grading)
- ◆ mixing
- ◆ shaping (pressing)
- ◆ drying
- ◆ firing

### 1.2.4 Types of Bonding

From the viewpoint of bonding, various methods are recognized which can be classified according to the temperature at which strength properties are developed, e.g.

- ◆ unfired products ( $<150^{\circ}\text{C}$ )
- ◆ fired at moderate temperatures ( $150\text{--}800^{\circ}\text{C}$ )
- ◆ fired at high temperatures ( $>800^{\circ}\text{C}$ )

and also according to the material nature of the bond, e.g.

- ◆ fireclay bond
- ◆ inorganic bond
- ◆ organic bond
- ◆ hydraulic bond
- ◆ ceramic bond

Since the bonding in many refractory materials tends towards ceramic bonding at operating temperatures, it is necessary to state that the previous classification of refractory material bonds is based on products coming from the supplier ready to be put into the kiln.

Examples of the bonding types encountered in refractories commonly supplied to the cement industry are given in Table 4.

**Table 4 Examples of the Various Material Bonds**

Nature of bond	Refractory Type	Characteristics
CERAMIC (Eutectic)	Fireclay bricks High-alumina bricks Silicate bonded magnesite bricks	The brick is first heated up above the eutectic temperature of the naturally present <u>bonding oxides</u> , and the structure formed by the liquid on cooling bonds the principal components together
CERAMIC (High fired)	High fired mangesia spinel bricks	The principal components are "dry" bonded by the use of very high temperatures (1700 - 1850°C), which causes the principal solid components to react directly with one another
INORGANIC	Phosphate-bonded alumina bricks	The bricks are bonded by chemical reaction between the added bonding agents (e.g. phosphates, sulfates, chlorides, chromates) and the bricks components at temperatures up to 150°C
HYDRAULIC	Refractory castables Gunning mixes	The refractory materials are bonded by a hydraulic calcium aluminate cement, just like normal concrete

#### 1.2.5 Shaped Insulating Refractory Products

These are shaped products having the same chemical classification as dense shaped refractories (see Table 1) but having a total porosity of at least 45 %. They are further characterized (ISO 22451972 E) by the temperature at which they do not display a permanent linear change of above 2 %, and by their bulk density. Such products are also known as lightweight insulating refractories and are mainly used as insulating backing in the heat exchangers of dry process kilns.

#### 1.2.6 Prepared Unshaped Dense and Insulating Refractories

These are prepared mixtures which contain an aggregate and a binder ready for use either

- ♦ as supplied e.g. ramming mixes
- ♦ after addition of suitable liquids  
e.g. refractory castables

These may be either dense or insulating, the latter requiring a porosity of  $\geq 45$  %.

Such materials be used for the following purposes, with further subdivisions being recognized within each group.

**Table 5: Categories of Unshaped Refractories**

<p><b>MONOLITHIC CONSTRUCTION/ REPAIRS</b></p>	<p>Ramming mixes delivered in a pliable non-coherent state and first harden upon heating</p> <p>Moldable mixes delivered in a plastic form and harden upon heating</p> <p>Refractory castables delivered dry Setting and hardening occurs without heating after mixing H<sub>2</sub>O or other liquids</p> <p>Gunning mixes delivered in a non-coherent state, suitable for placing by pneumatic projection</p>
<p><b>MORTARS/ JOINTING MATERIALS</b></p>	<p>Refractory cements these are placed wet, and harden at high temperature by ceramic bonding</p> <p>Refractory cements (hydraulic binder) as above but harden without heating</p> <p>Refractory cements (chemical binder) harden by chemical reaction at lower temperatures than required for cement bonding</p>

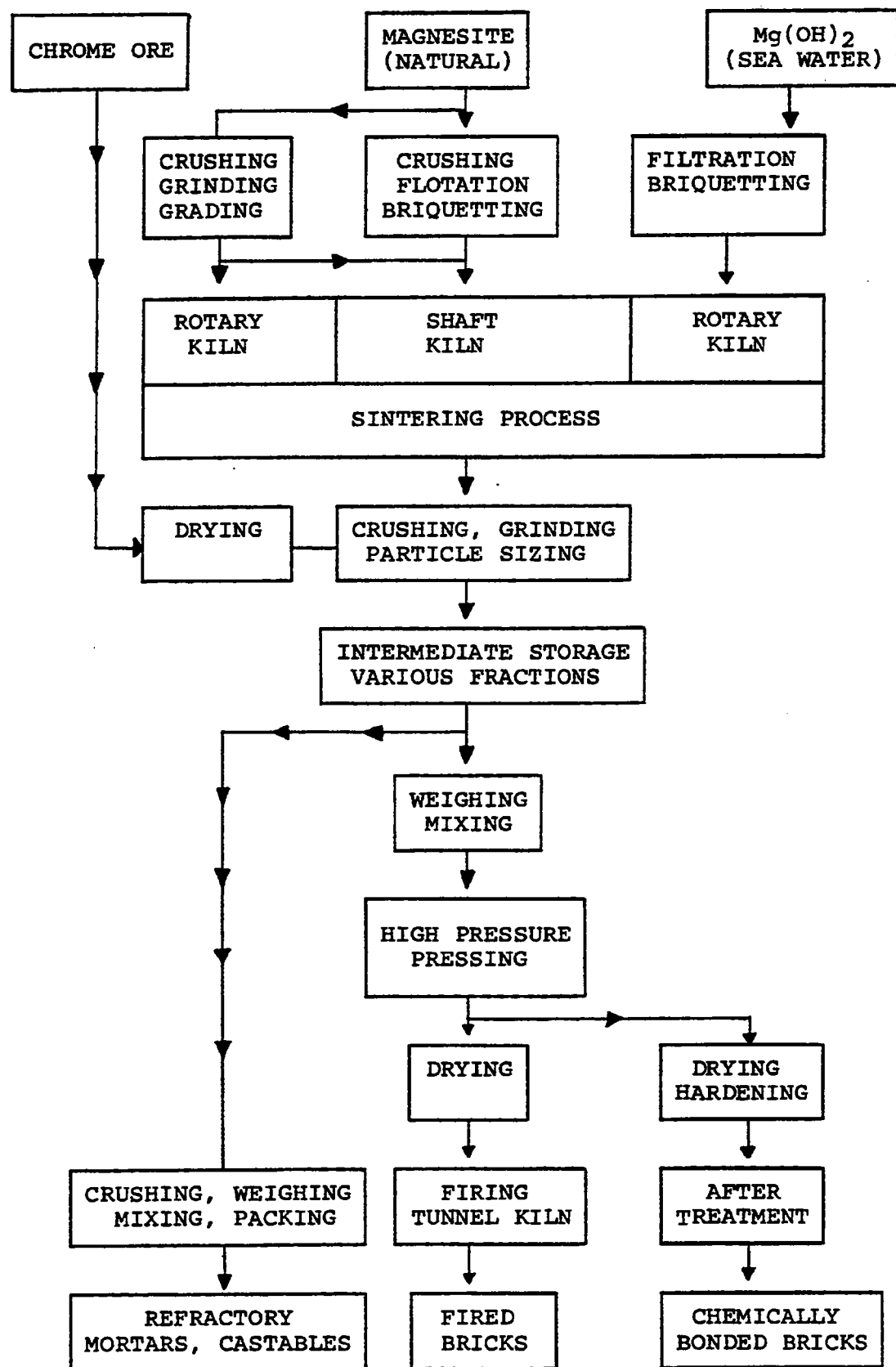
### 1.3 Manufacture of Refractory Products

#### 1.3.1 Manufacturing Process

A typical flowsheet for the production of shaped and unshaped magnesite based refractories is shown in Fig. 2. As can be seen, the process can be split into four principal stages including

- ◆ preparation of sintered magnesia and dried chromite in defined particle size ranges
- ◆ preparation of mix having specific proportions of the various magnesite and chromite fractions
- ◆ pressing of required format (shaped refractories)
- ◆ bonding process (direct, eutectic, chemical)

Fig. 2 Flow Diagram for the Production of Shaped and Unshaped Magnesite Based Refractory Products



As can be seen, the magnesite sinter may originate from either natural magnesite or from  $\text{Mg(OH)}_2$  extracted from sea water. To produce the latter, sea water containing about 200 g  $\text{MgO}/100$  liters is reacted with slaked lime slurry to precipitate  $\text{Mg(OH)}_2$ . The resulting slurry is filtered to produce a paste which is calcined at  $900\text{--}950^\circ\text{C}$  to form "caustic calcined magnesite". This is then fed through briquetting rollers to press dry, dense tablets, which are then dead burnt at  $1800^\circ\text{C}$  in rotary kilns. During the burning process, the undesired  $\text{B}_2\text{O}_3$  content of the  $\text{MgO}$  is appreciably reduced. In the production from natural magnesite, impurities such as dolomite are removed by floatation after crushing. From the dead burnt sinter the coarser fractions are then prepared by crushing and sieving, with the finest being prepared by subsequent milling.

By using different sizes of sinter and chromite in various proportions, and controlling the total porosity and pore size distribution, a variation of refractory properties may be achieved.

### 1.3.2 Source of Materials

The production of refractory materials was originally located in areas near to iron works where clay deposits were available with a sufficiently high  $\text{Al}_2\text{O}_3$  content to allow the production of fireclay bricks. With the development of refractories to include high alumina, magnesite, magnesite chrome, and most recently periclase spinel types, the raw materials are not available in the traditional production areas and have to be purchased on the international market. The refractory manufacturer therefore cannot always produce his product with materials from the same source.

Of the various materials of a grade suitable for refractory production, the most well known sources are indicated in Table 6.

**TABLE 6 Sources of Raw Materials for Refractory Production**

Raw Material	Source	
For Basic Refractory Products	Country	Location
<u>Magnesite</u>		
• coarse crystalline(natural)	Austria Canada	Radenthein Veitsch Radium Hot Spring
• crypto crystalline(natural)	Greece Turkey Yugoslavia India Australia South Africa	Euboea
• sea water (synthetic)	Italy England Ireland Japan USA	Sardinia Hartlepool Drogheda
<u>chrome ore</u> (natural)	Philippines Turkey South Africa Greece Iran	Transvaal
<u>magnesia spinel</u> (synthetic)	Japan England Germany	

The key factor deciding whether a raw material can be used for refractory production is the content of the minor oxides, i.e.  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  which, when they are present in excessive quantities, lead to a reduced refractoriness. Synthetic raw materials (e.g. sea water magnesite) are often too pure and have to have their composition modified by the use of additives to control their  $\text{CaO/SiO}_2$  ratio and hence improve their sintering behavior.

Although the critical composition limits at which a manufacturer accepts or rejects a specific raw material are not made available and remain a trade secret, typical compositions of acceptable materials are as indicated in Table 7.

**Table 7 Typical Compositions of Raw Materials**

Material	Chemical Composition (wt %)						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Cr <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
BAUXITE (sintered)	6.2	86.9	1.8	0.04	0.08	--	2.7
CHROME ORE	5.4	20.4	18.4	0.6	18.1	37.0	--
DOLOMITE (sintered)	2.3	1.0	0.8	58.8	36.2	--	0.2
MAGNESITE (sea water- sintered)	0.4	0.2	0.6	0.9	98.1	--	--
MAGNESITE (raw)	2.1	0.6	1.5	2.1	93.6	--	--

### 1.3.3 Production Details

Production details for the manufacture of refractories are seldomly made available. The following points, however, give an indication of typical layout and performance of a refractories plant, which receives already sintered raw materials (see Table 8).

**Table 8 Production Details**

No of silos per component:	up to 4 for various size fractions
Weighing and mixing process:	usually automatically controlled by computer. Proportions change with brick types and material source
Brick presses:	1500 T total pressure, fully automatic operation. Often up to 5 presses/plant
Tunnel oven (for firing):	capacity 30'000 t/y
Firing data:	time up to 3 days temperature 1550 - 1850°C heat consumption 1500-2000 kcal/kg



## 1.4 Testing of Unused Refractories

### 1.4.1 General

Refractory products are routinely tested at several stages during their manufacture and in some industries (e.g. steel production) are even tested by the user prior to delivery before actually being put into service. Testing may be considered as falling into the following categories and fulfilling the indicated functions.

**Table 9      Testing of Unused Refractories**

Type of testing	Purpose
Manufacturers Process and Quality Control	Check on Production Process/Equipment/Operations
Standard Refractory Tests (e.g. DIN, ASTM, etc.)	To ensure that product meets manufacturers description
Non-Standard Tests (e.g. at HMC)	To assess whether product is suitable for operations in the specific user industry
Users Acceptance Quality Control	Check whether delivered refractories meet manufacturers specifications or are suitable for users specific requirements

Whereas in the cement industry the used standard ASTM, DIN, BS tests are considered as giving a not unreliable indication of the performance of the mortar or concrete in service, the prescribed standard tests for refractories are not specific for clinker production conditions. It has even been suggested that it would be more useful to test refractories that had already been in service, and not new unused refractories, and so obtain a practice related indication of the suitability of refractories under clinker production conditions.

### 1.4.2 Manufacturers Process Control

Upon delivery, the refractory manufacturer checks the chemical composition of the supplied chrome ore, sintered magnesite, dolomite, bauxite etc. to ensure that the levels of the minor oxides, e.g.  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , do not exceed the requirements for the refractory type concerned (e.g. direct or indirect bonded basic bricks). In the case of sea water magnesite the boron content is checked, as is the loss on ignition in the case of sintered dolomite, which must be used within approximately 48 hours of delivery.

During the mixing process, the granulometry of the various fractions of each component (e.g. chrome ore, magnesite) is routinely checked as is the mixing ratio of the raw components. These checks are especially necessary when more than one type of for example magnesite-chrome brick are being simultaneously produced. In larger production plants, quality control samples are taken on a statistical basis and are sent to the quality control laboratory. In several companies, all the quality control and production data are stored in a computer databank, thus allowing the production history of any specific delivery to be easily recalled.

In the most modern production lines, the whole process is fully automated from component mixing to packing. After pressing, each unfired brick is automatically checked for its dimensional accuracy, whilst the weights are checked only on chosen samples. After firing, the bricks are all individually tested automatically for dimensions, and by a controller who checks for various subjective factors. The following table lists typical factors evaluated in the subjective tests:

Table 10 Criteria for "Optical" inspection of Refractory Bricks

OPTICAL INSPECTION OF FIRED REFRACTORY BRICKS			
Date: 9.3.95		Manufacturer: Mino Yogyo	
Brick Type: CF-83S		Format: ISO 320	
No. of Bricks Tested: 1			
<b>CLANG TEST</b>			
Clang Response	tense	normal	dull
(using small hammer)	1		
<b>APPEARANCE</b>			
Aspect	none	subjective impression	
		insignificant	significant
broken corners	1		
broken edges	1		
popouts/holes	1		
melting	1		
irregular surface	1		
cracking	1		
peeling	1		
<b>TEXTURE</b>			
Texture	normal/homogeneous	cracking	inhomogeneous
broken section			
cut section	1		
numbers refer to individual bricks			
<b>ATTACHMENTS</b>			
Aspect	comment		
steel plate			
correct face	yes		
accurately placed	yes		
excessive glue	no		
cardboard			
correct face	yes		
accurately placed	yes		
excessive glue	no		
<b>MARKINGS</b>			
stamped/ colouring	yes		
brick type	yes CF-83S		
format	yes ISO 320		
production data	yes 61		
Lotus\reports\inspect			

### 1.4.3 Standard Refractory Tests

The product description of refractories is defined in terms of various standard test methods (ASTM, BS, DIN, ISO) which measure their chemical composition and physical properties. Testing is performed both at room and elevated temperatures and for shaped refractories includes the following:

**Table 11 Standard Tests for Refractory Materials**

Temperature	Property	Standard		
		ASTM	BS	DIN
Ambient	Dimensions	C-134	1902	
	Density	C-134	1902	51'065
	Porosity	C-20	1902	51 '056 51'058
	Cold crushing strength	C-113	1902	51'048 51'067
	Chemical composition	C-572, 573,574	1902	51'070
Elevated	Pyrometric cone equivalent	C- 24	1902	51'063
	Hot rupture modulus	C-583	1902	51'048
	Refractoriness under load	C-16	1902	51'053
	Creep in compression		1902	51'053
	Thermal expansion	C-832	1902	51'045
	Permanent linear change	C-113	1902	51'066
	Shock resistance	C38, 107,122	1902	51'068
	Thermal conductivity	C-201, 202	1902	51'046

Testing procedures have also been established by ASTM for unshaped refractories and include the following in addition to those applicable for shaped products:

- ◆ workability index (C-181)
- ◆ dry firing shrinkage (C-179)
- ◆ cold bond strength

It should be appreciated, however, that various test methods supply data which cannot be numerically compared with that obtained by another standard test method, e.g. thermal conductivity. This must be kept in mind when selecting refractories from international suppliers, who often define the quality of their product according to their national standards. A higher catalogue value does therefore not always necessarily imply a higher quality product, and makes a rational selection even more difficult. To avoid such difficulties, international standard specifications are in the process of being established, but progress in this direction has been slow. So far only test procedures for Pyrometric Cone Equivalent (ISO R 528) and refractoriness under load (ISO R 1893) are internationally defined. Test procedures for high temperature modulus of rupture, bulk and true density, and permanent linear change have reached a "draft international standard" status. For the majority most important properties no international standard yet exists.

The previously listed standard tests, although they do to a moderate extent indicate the general performance of a refractory, are not wholly specific for conditions representative of those encountered in cement rotary kilns. It is therefore not surprising that in the cement industry no detailed generally known and accepted guidelines have been established for the exact properties of the refractory types required in the various kiln zones.

Although qualitative rather than quantitative, a hypothetical relationship can be proposed (Table 12), indicating which physical and chemical properties exert an influence on the rate of wear by the common mechanical, thermal and chemical wear factors. From this it can therefore be deduced that the standard tests are more suited for determining the resistance to mechanical attack, less for thermal attack, and almost no indication against resistance to attack by chemical influences.

**Table 12      Significance of Characteristic Refractory Properties for In-service Life Expectancy**

SIGNIFICANCE CHARACTERISTIC	WEAR FACTORS								
	MECHANICAL			THERMAL			CHEMICAL		
	TH. STRESS	STRESS	ABRASION	OVERHEATING	SHOCK	FATIGUE	INFILTRATION	ALKALI CONDENSATION	PO <sub>2</sub> , SO <sub>3</sub> , CO <sub>2</sub>
DIMENSIONS / ACCURACY	●								
DENSITY			○						
POROSITY			○		○		○	○	
COLD CRUSHING STRENGTH	●	●	●						
CHEMICAL COMPOSITION				○			○		
REFRACTORINESS				○					
HOT RUPTURE MODULUS	●	●							
THERMAL EXPANSION	●				○				
PERMANENT LINEAR CHANGE	●								
SHOCK RESISTANCE					●				
THERMAL CONDUCTIVITY									

#### **1.4.4 Non-Standard Tests**

As a means of assessing the performance of refractories under more practice related conditions, almost all manufacturers have developed their own non-standard test procedures. These include methods for the determination of

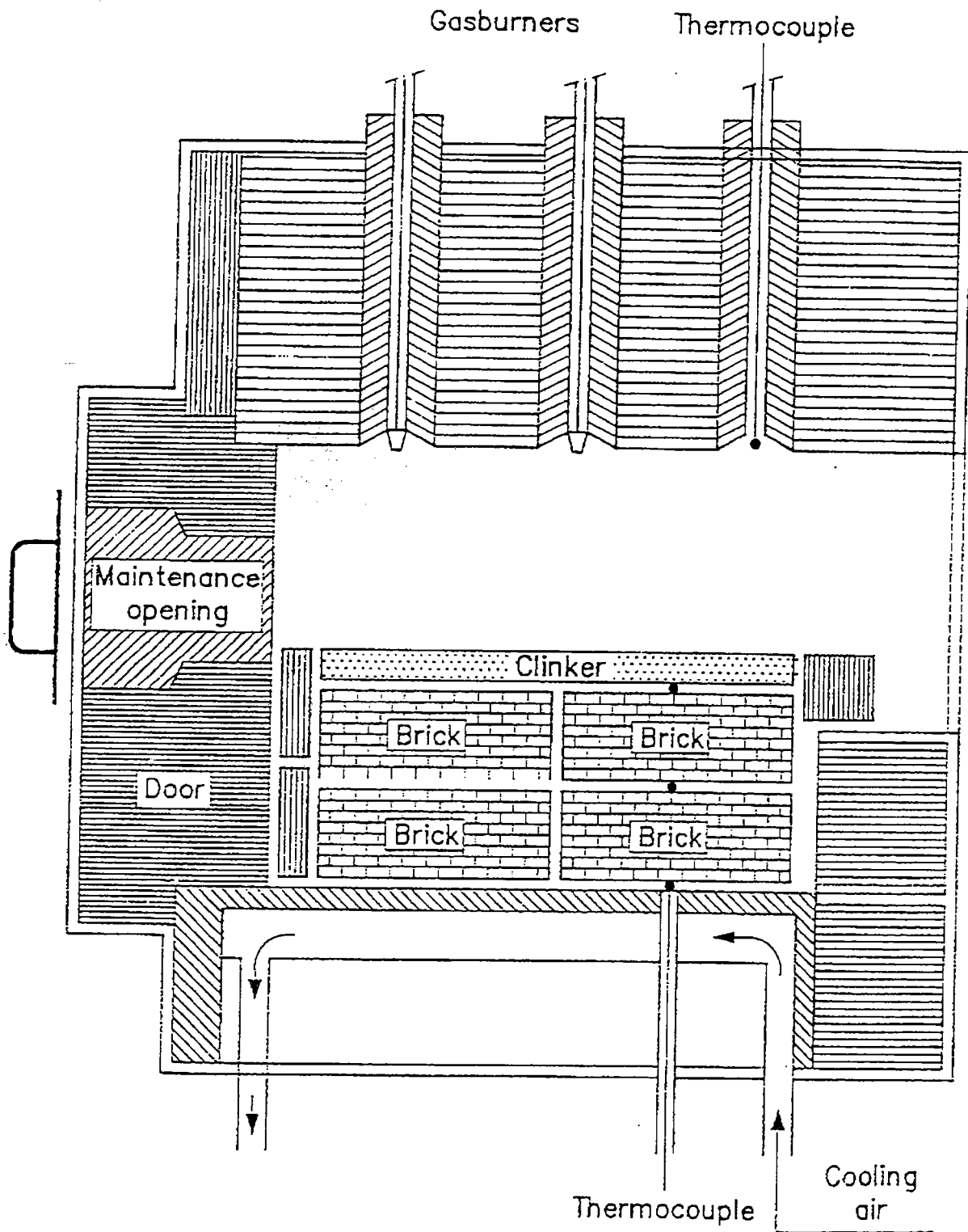
- ◆ coating adhesion thermal
- ◆ shock resistance
- ◆ resistance to alkali attack

all of which can be tested by not too complicated test procedures.

#### **1.4.5 Sinterzone Coating Adhesion**

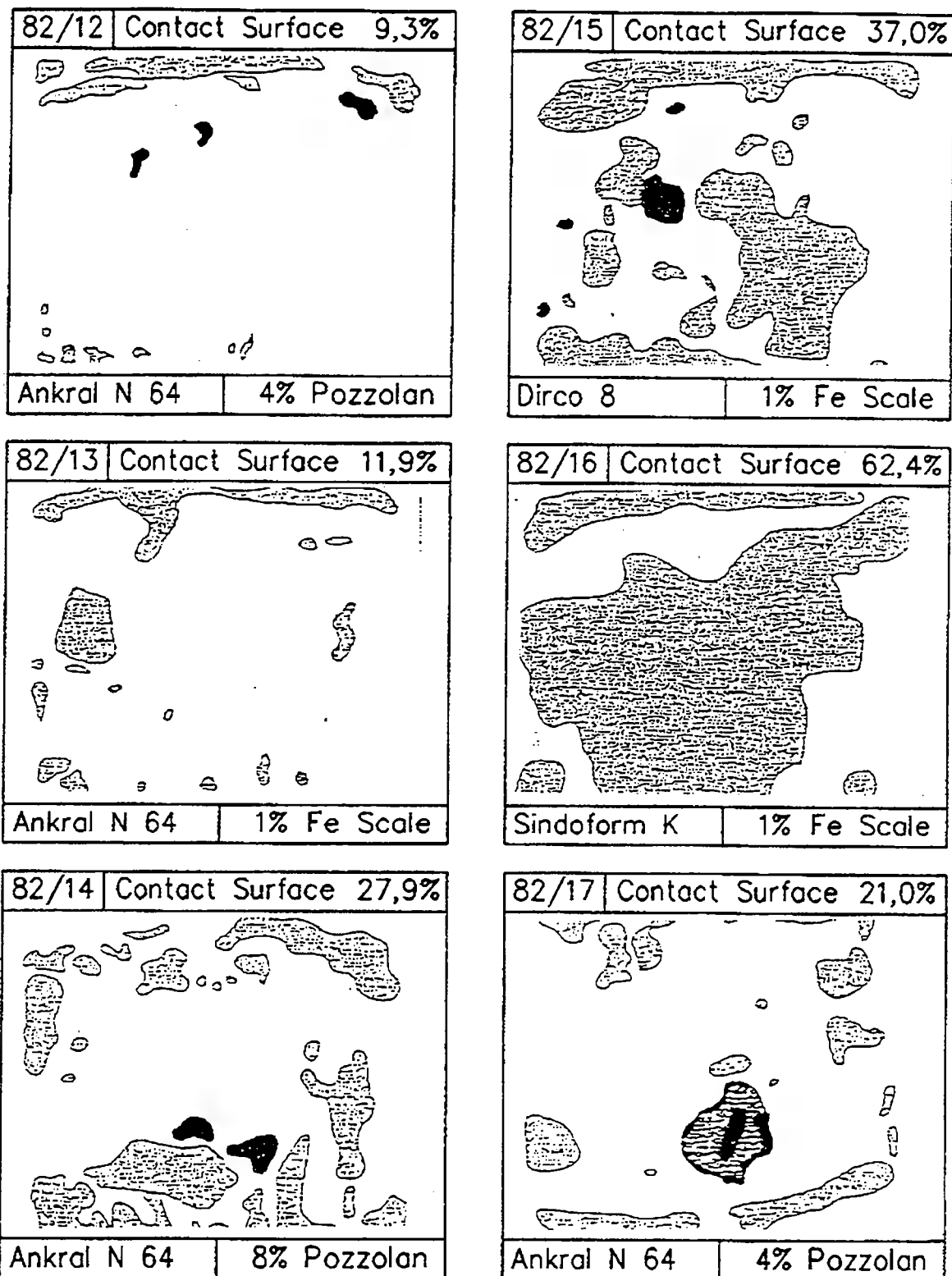
The tendency towards coating adhesion can be determined at HMC/MA by means of its own recently developed Fig. 3, and fully described in various publications. In developing this method, all the previously developed procedures were evaluated, their deficiencies eliminated and their advantages combined in a single large scale laboratory method.

Fig. 3: Coating Test Furnace - Longitudinal section



Examples representative of the type and degree of various observed contact surfaces obtained by this method are given in Fig. 4.

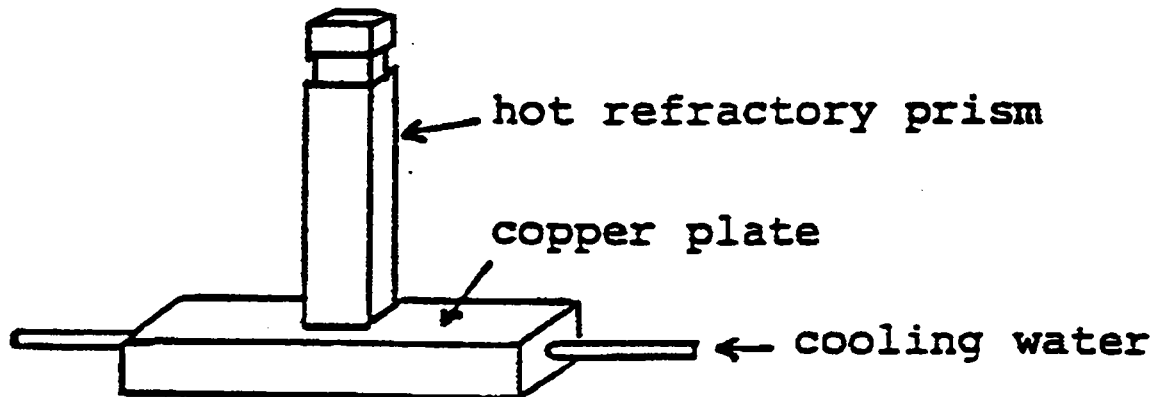
Fig. 4: Typical Contact Zones in Coating Zones



#### 1.4.6 Thermal Shock Resistance

A simple, but extremely aggressive thermal shock resistance test, employed internally in the German steel industry, requires a heated prism of the refractory material under test to be placed on its end on top of a water cooled copper plate (see Fig. 5).

**Fig. 5**                    **Arrangement of VDEhL Thermal Shock Test**



This test is considered to be more practice relevant than the temperature shock caused by spraying the complete refractory test piece with water or air, conditions never encountered in practice. The test, because only one end of the refractory material is cooled, is said to be much more demanding than either of the two DIN methods and at the same time more practice-like.

#### 1.4.7 Alkali Attack

To determine the resistance of high alumina refractories to alkali attack, many manufacturers use a modified form of the DIN 51'069 test procedure originally developed for testing the resistance of refractories to blast furnace slags. In this method 50 mm diameter x 35 mm deep holes in the test pieces are filled with  $K_2CO_3$  and the material heated for 5 hr. at 1100°C. After cooling, the test samples are cut with a diamond saw and attack judged according to depth of penetration and to whether the bricks show cracking or not. Examples showing a weak and a strong resistance to attack by this simple test method are shown in Figs. 6a and 6b.



**Fig 6a      Strong Alkali Attack**

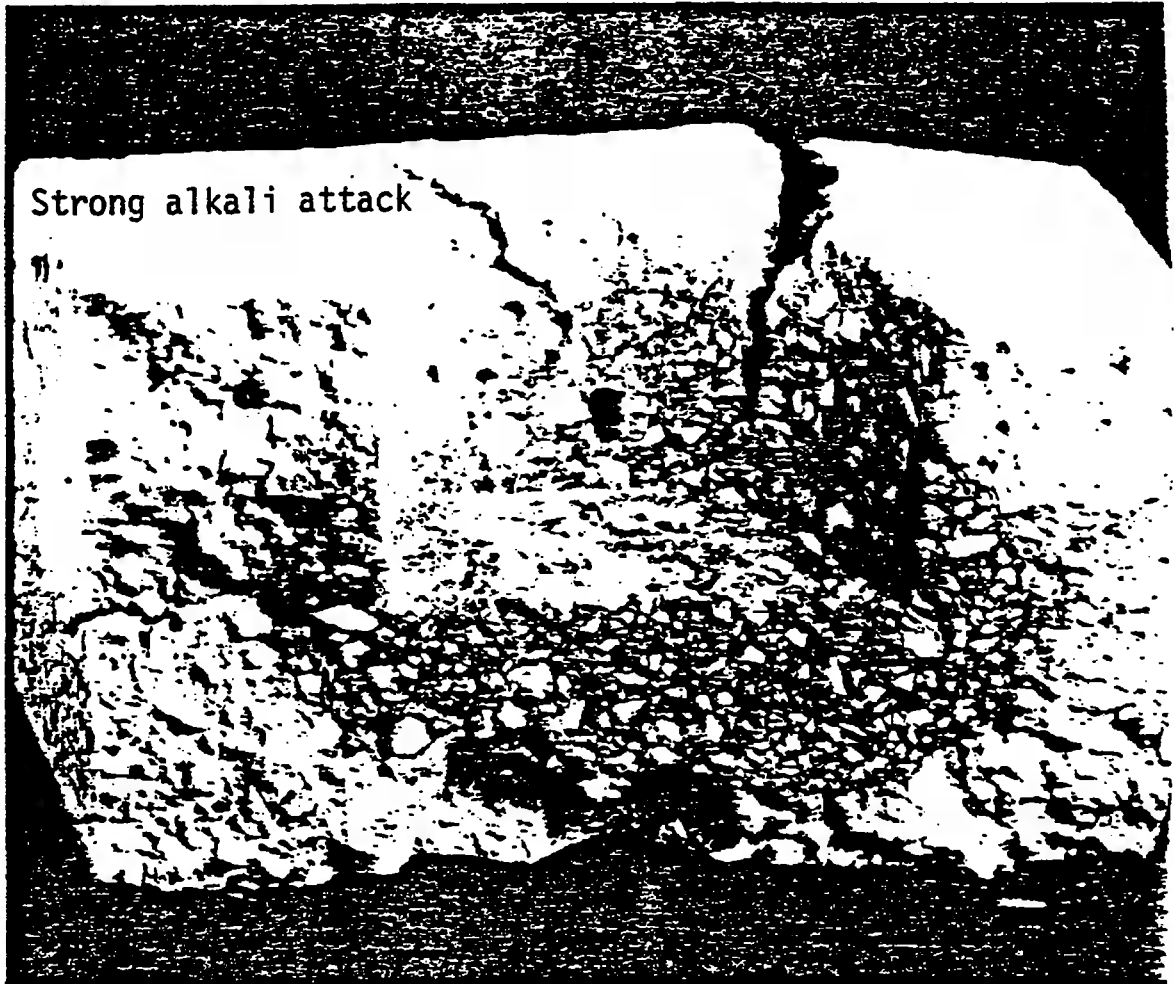
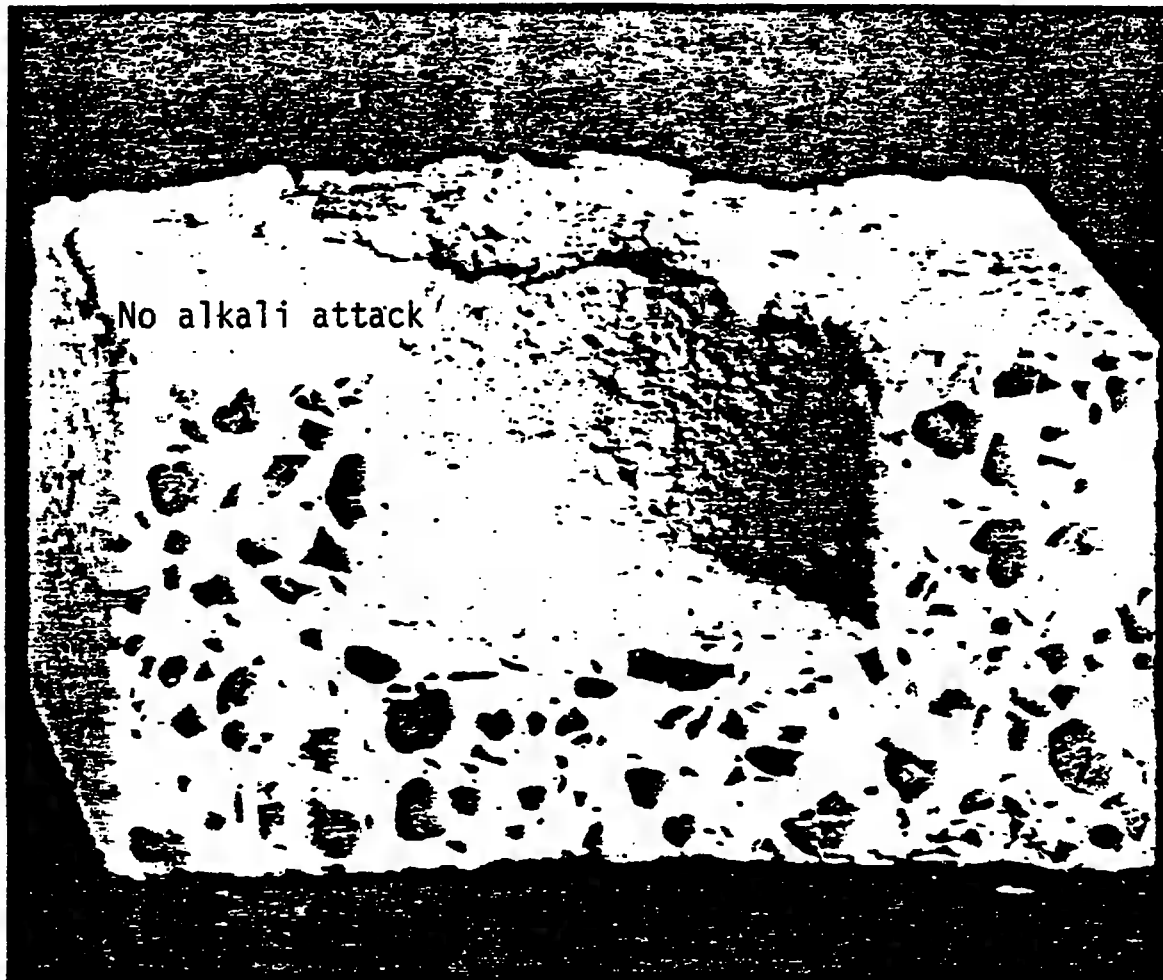


Fig 6b

No Alkali Attack



#### 1.4.8 Acceptance Testing Criteria

Although acceptance testing of refractories is not practiced in the cement industry, this is not the case in steel. Refractories are not, however, tested just for testings sake, but are viewed from the aspect of their costs and from the demands placed upon them, and quality control testing carried out accordingly. A principal objective of quality control is to prevent cases of failure in sensitive aggregates which in addition to immense financial consequences may in the steel industry also endanger human lives.

For the cheaper refractory grades, for less critical applications, the manufacturers data sheet specifications and quality control are accepted, with no essential input on the part of the user. Simple optical inspection of the state of the delivered materials is considered as being sufficient. Even for moderate cost refractory grades in service under moderately critical applications, testing is confined to carrying out spot checks, after delivery, on random samples, determining such conveniently measurable properties as dimensional accuracy, cold compressive strength. The results are collected to detect trends over long periods and are also if anomalous communicated to the supplier, for the latter's "information".

Only for applications for which the refractory properties are critical are quality control examinations carried out systematically on a statistical basis. In such cases, the refractories are controlled prior to dispatch from the suppliers plant and checked according to specifications and tolerance limits previously agreed upon between supplier and client. The chosen test samples are normally divided into 2 sub-samples, one portion being tested in the supplier's laboratory, the other in the user's. This class of refractory is ordered well in advance of the specified delivery date e.g. 6 months, and this long range planning assures that the material to be supplied lies within the acceptance limits. The costs for statistically significant quality control are borne equally by supplier and user and often involve 3 - 4 man days working time for a quantity of 150 - 200 tons, the costs corresponding to 1.5 % of the delivery value.

### 1.5 ZONING of Cement Kilns

Because the refractories in the cement kiln have to perform several duties, as already listed in 1.1, no single refractory type can now fulfill all the requirements. As factors such as

- ♦ the changing temperature profile in the kiln
- ♦ the changing physical and chemical nature of the kiln feed ranging from raw meal to clinker

must be taken into consideration, the zoning of the kiln, with respect to the refractory lining, is a necessity. Indeed in some kiln zones it is normal to have two refractory types at any one position, namely a "working lining" and a backup insulating lining.

In a commonly established practice, the kiln zones are defined according to the changes occurring in the kiln charge as indicated in Table 13.

**Table 13 Characterization of the Various Kiln Zones**

Kiln Zone	Process	Material Change	Temp.Range
Drying	Wet and semi-wet	Expulsion of slurry or nodule moisture	$\leq 100^{\circ}\text{C}$
Preheating	Wet and dry	Expulsion of chemically bonded OH groups	$100-700^{\circ}\text{C}$
Calcining	"	Expulsion of $\text{CO}_2$ from carbonates	$600-900^{\circ}\text{C}$
Transition	"	Formation of intermediate and clinker minerals	$900-1350^{\circ}\text{C}$
Sintering	"	Granulation of clinker and formation of permanent coating	$\geq 1350^{\circ}\text{C}$
Discharge	"	Cooling of clinker within kiln	$1400-1250^{\circ}\text{C}$

Variations to the previous scheme include the definition of a chain zone (i.e. a combined drying and preheating zone) and the division of the transition zone into the safety zone and the transition zone, often described as the upper and lower transition zones.

In Figs. 7 and 8 a typical zone plan can be seen for wet and dry process operations with indications of the kiln temperature and various types of attack to be expected.

Fig. 7 Typical Rotary Kiln Data - Dry Process

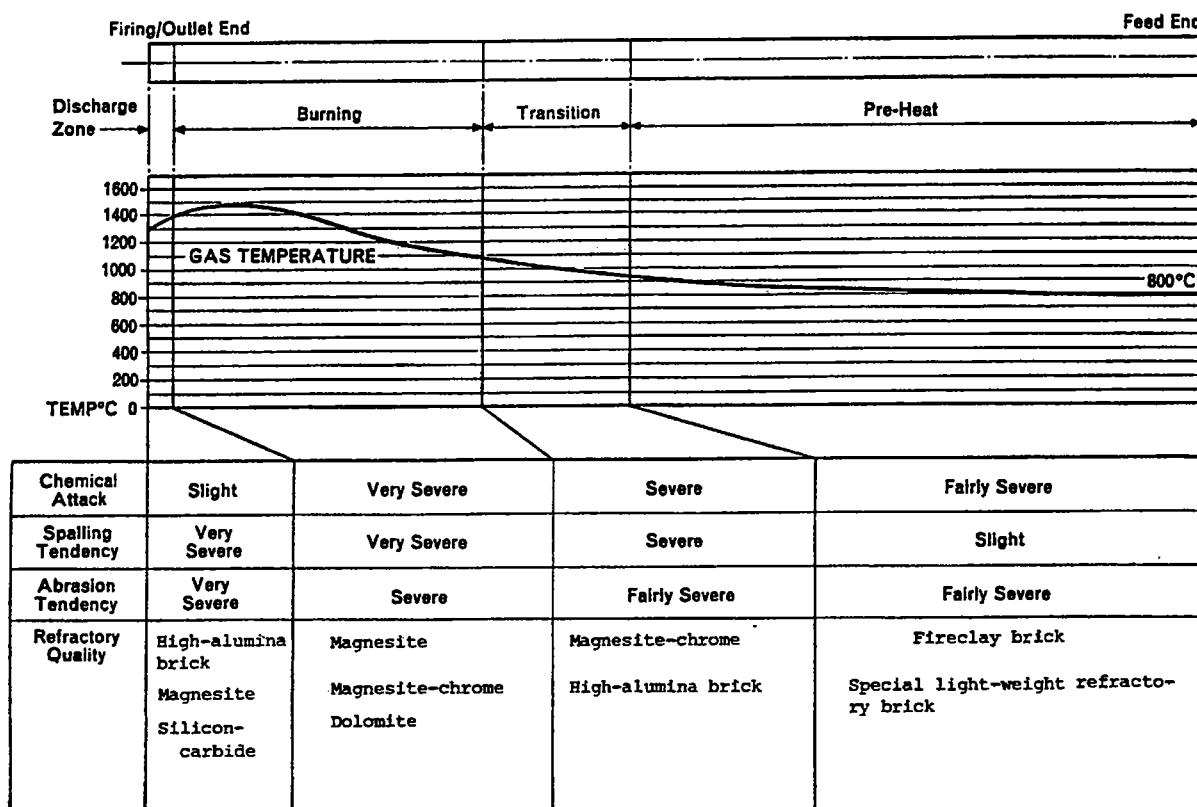
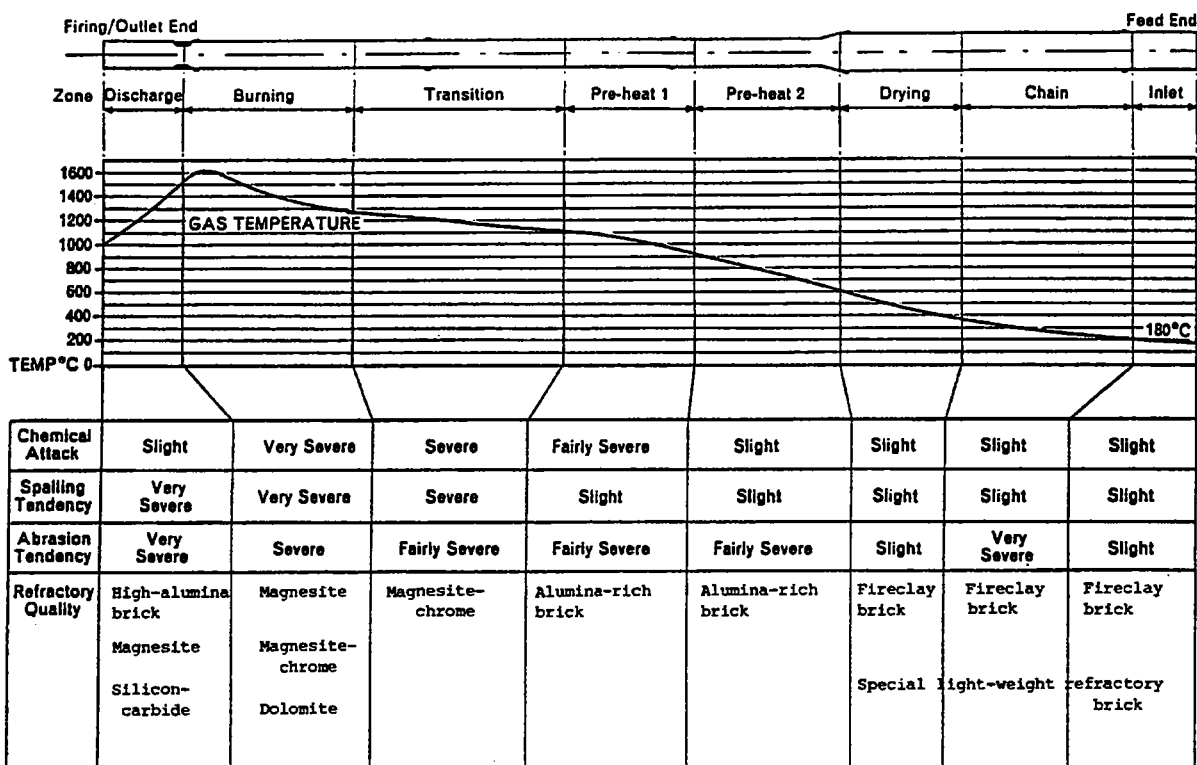


Fig. 8 Typical Rotary Kiln Data - Wet Process



## 1.6 Wear of Kiln Refractories

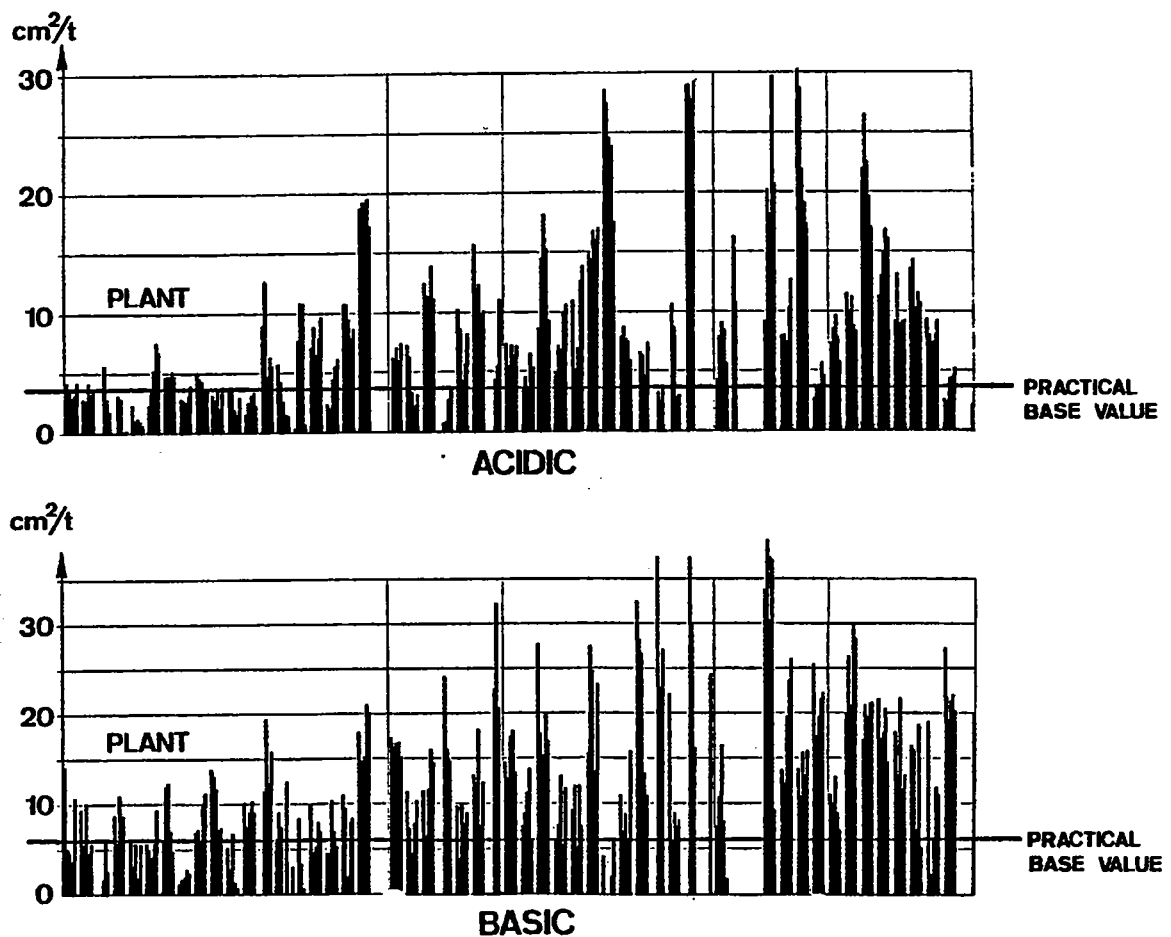
### 1.6.1 General

Even under the most favorable operating conditions, refractory linings are subject to a definite measurable rate of wear. Based on plant experience (Fig. 9), the minimum consumption rate achievable in practice, for basic and acidic types may be considered as follows:

- ◆ basic refractories  $\approx 6 \text{ cm}^2/\text{t}$  clinker
- ◆ acidic refractories  $\approx 4 \text{ cm}^2/\text{t}$  clinker

It should be considered that these values are average values for the total basic and acidic linings and that at various positions inside the kiln both higher and lower specific consumption rates are observed. Whereas some plants can consistently approximate to these desired low consumption rates, in most cases refractory consumption is higher with average consumption rates of  $30 \text{ cm}^2/\text{t}$  clinker and above being not uncommon.

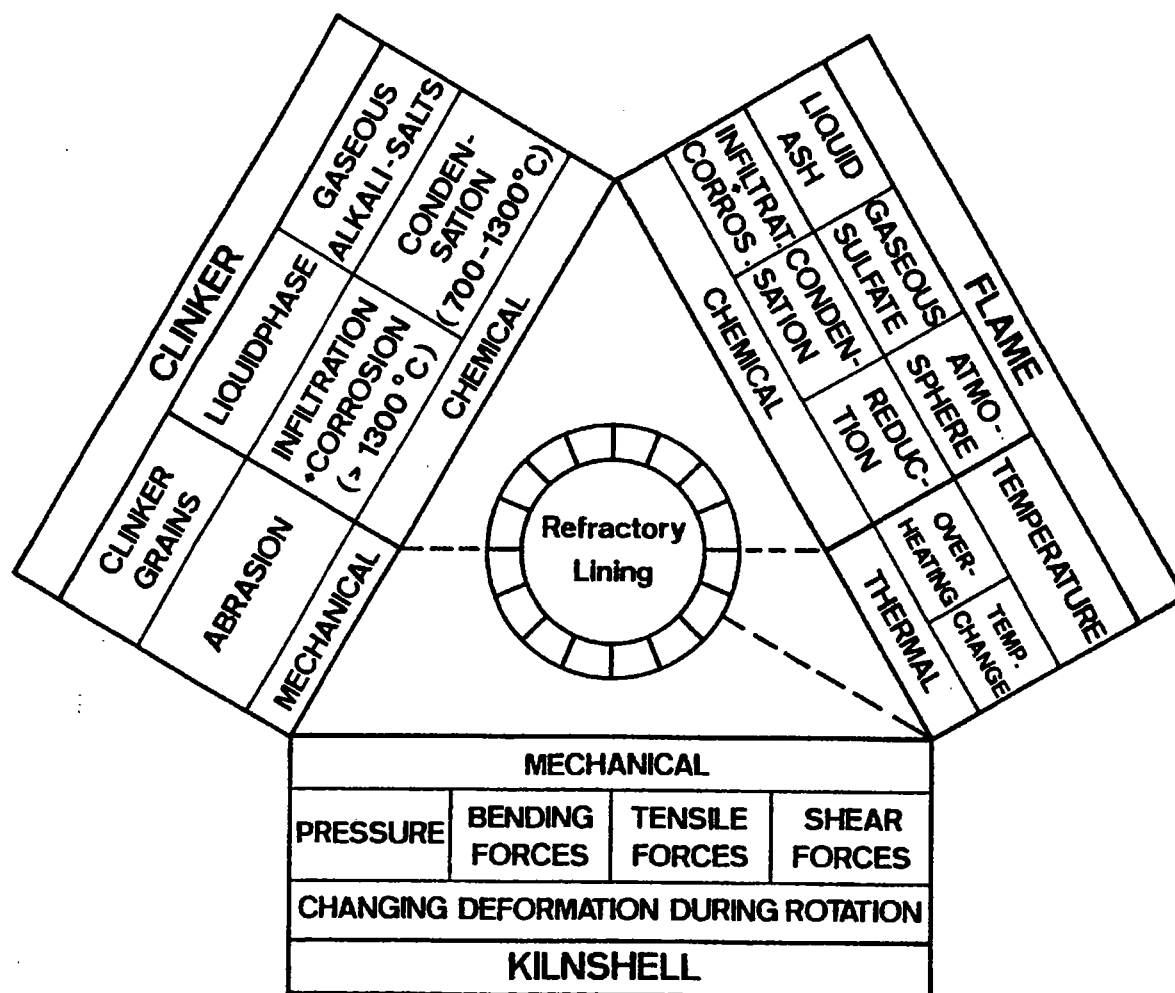
**Fig. 9 Consumption of Kiln Linings**



### 1.6.2 Causes of Wear

The principal causes of wear may be attributed to thermal, mechanical or chemical factors, acting either alone or more frequently in combination. Details concerning these various wear types are given in Fig. 10.

**Fig. 10** Influence of chemical, thermal and mechanical factors on kiln refractory linings



Depending on the period for which observations are based it can be observed that the frequency of wear, due to any particular mechanism, is not constant but varies. This can be seen in Fig. 11 showing the frequency of the wear mechanisms from 1964 - 1968 and from 1968 - 1974, i.e. since the introduction of large diameter process kilns. As can be deduced, the identified causes of wear before 1968 were principally chemical (silicate and alkali infiltration) in nature with mechanical and thermal factors being of equal but secondary importance. Between 1968 and 1974 mechanical stresses became by far the principal failure cause, with chemical and thermal being of equal importance. Whereas before 1968 the causes could clearly be identified in only 50 % of the investigated cases, the percentage of those not identified dropped to 25 % between 1968 and 1974.

Although no statistics are presently available, the principal causes of wear may again be chemical in nature, originating from silicate attack and reducing conditions stemming from the widespread reintroduction of coal firing.

**Fig. 11 Main Causes of Wear In Sintering Zones**

EXAMINATIONS BEFORE 1968  AND 1968-74

CAUSE OF WEAR	EXAMINATIONS		
	NUMBER	%	
OVERHEATING	10	10	<div><div style="width: 10%;"></div></div>
SILICATE INFILTRATION	11	10	<div><div style="width: 11%;"></div></div>
ALKALI INFILTRATION	16	15	<div><div style="width: 16%;"></div></div>
THERMAL SHOCK	8	8	<div><div style="width: 8%;"></div></div>
MECHANICAL STRESS (THERMAL EXPANSION • KILN SHELL)	26	24	<div><div style="width: 26%;"></div></div>
MISCELLANEOUS (NOT DETERMINED, CANNOT BE CLASSIFIED)	35	33	<div><div style="width: 35%;"></div></div>
	<b>106</b>	<b>100</b>	

### 1.6.3 Mechanisms by which Damage Occurs

The chemical, thermal and mechanical factors responsible for wear cause changes to occur in the refractory materials by means of material transport stress and erosion. This results in either a modification or a destruction of the refractories texture leading to discontinuous wear by spalling, or to a continuous wear by abrasion. The relationship between these factors are indicated in Fig.12.

Fig. 12 Characterization of Wear Magnesite-Type Linings

WEAR-TYPE	COATING PRESENT (INSTABLE)	COATING ABSENT TOO HIGH   TOO LOW TEMPERATURE		CAUSES		
				MATERIAL TRANSPORT	STRESS	EROSION
<b>CHEMICAL:</b> INFILTRATION, LIQUID CONDENSATION, ALKALIS REDUCTION	◐  ○	◑  ○  SPECIAL CASE	◒  ○	▨		
<b>THERMAL:</b> OVERHEATING THERMAL SHOCK HEAT FATIGUE	○ ● —	○ ◑ ◑	— ◑ ○		▨	
<b>MECHANICAL:</b> STRESSES EROSION	◑ ○	◑ ◑	◑ ●			▨
MECHANISM OF WEAR	DISCONT DETACHMENT OF COATING	CONT. (ALMOST) SPALLING AND ABRASION	CONT. ABRASION	MODIFICATION OF TEXTURE	DESTRUCTION OF TEXTURE	ABRASION
KILN ZONE	SINTER TRANSITION	SINTER (SOMETIMES)	DISCHARGE TRANSITION	EFFECT		

EFFECT ○ = VERY WEAK ◐ = WEAK ◑ = AVERAGE ◒ = STRONG ● = VERY STRONG

#### 1.6.4 Recognition of the Various Wear Causes

To help identify the cause or causes of refractory wear, a range of characteristics can be proposed summarizing the changes resulting from the various attack mechanisms. A list of these is presented in Tables 14a and 14b. As can be seen, many of the changes can be observed macro or microscopically or by chemical analysis, and so a preliminary conclusion as to why refractories have failed can often be drawn by plant personnel.



**Table 14a CHARACTERISTICS OF THE VARIOUS DAMAGE MECHANISMS FOR ACIDIC AND BASIC BRICKS**

♦ Chemical Damage

- *Liquid infiltration* (clinker / coal ash)
  - \* lower porosity due to penetration
  - \* change of colour
  - \* change of mineralogy
  - \* increase in CaO, SiO<sub>2</sub>, (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>)
- *Alkali condensation*
  - \* increases in Na<sub>2</sub>O, K<sub>2</sub>O, Cl, SO<sub>3</sub> levels
  - \* porosity decrease
  - \* presence of light coloured layers
  - \* alkali bursting (Al<sub>2</sub>O<sub>3</sub> refractories)
  - \* change of mineralogy
- *CO<sub>2</sub>/SO<sub>3</sub> attack (on CaO containing compounds)*
  - \* decrease of porosity
  - \* presence with white coloured layers
  - \* increase in CO<sub>2</sub>, SO<sub>3</sub>
  - \* change of mineralogy

**Table 14b CHARACTERISTICS OF THE VARIOUS DAMAGE MECHANISMS FOR ACIDIC AND BASIC BRICKS**

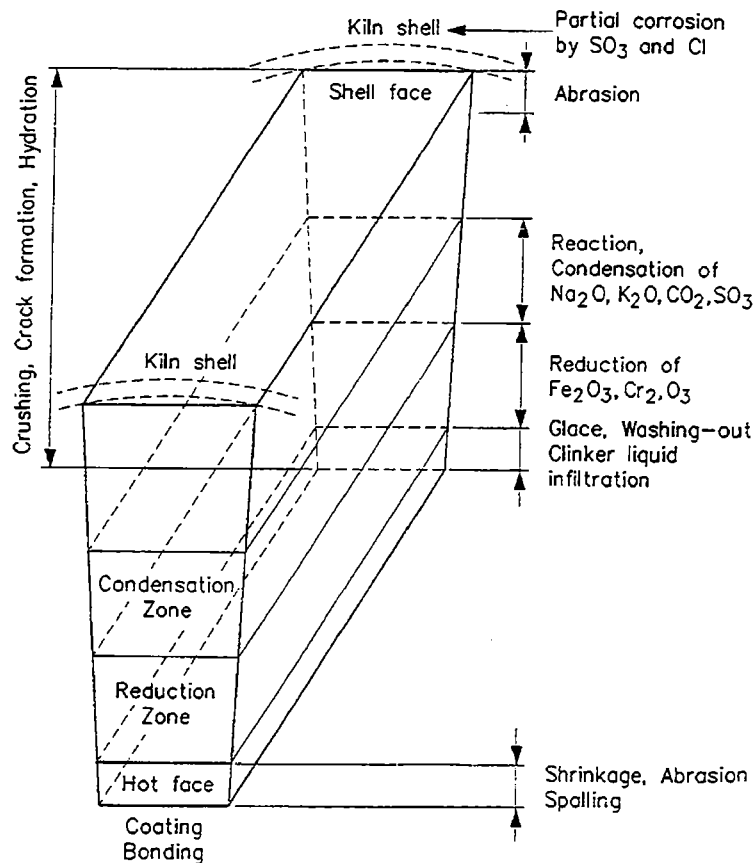
♦ Thermal damage

- *Overheating*
  - \* melting of hot face
  - \* change (increase / decrease) in type of porosity
  - \* elongation of periclase crystals
  - \* reduction of chrome content
  - \* diffusion of low melting silicates, aluminates
  - \* change of colour
- *Shock*
  - \* spalling of hot face

♦ Mechanical damage

- *Kiln deformation / thermal expansion*
  - \* porosity unchanged
  - \* chemistry / mineralogy unchanged
  - \* spalling over wide areas
  - \* crack formation on micro to macro scale

## Appendix 2: A graphical representation of the damage zones



### 1.7 Chemical Reactions Producing Refractory Damage

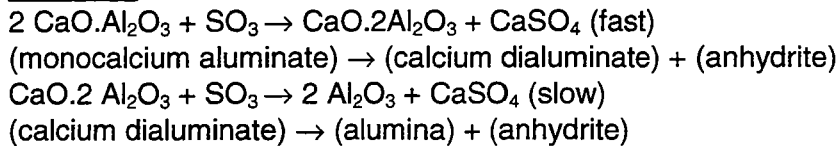
The chemical reactions occurring when refractories are attacked by siliceous or alkali sulfate infiltration's or by reducing atmospheres have been thoroughly investigated. Examples will now be given of those reactions occurring at various positions in the kiln.

#### 1.7.1 $\text{SO}_3$ Attack on Castables in Heat Exchangers

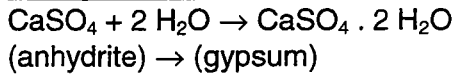
The bonding agent of many refractory castables is monocalcium aluminate (CA) which exhibits both hydraulic properties (e.g. high alumina cement) and a high melting point ( $> 1600^\circ\text{C}$ ). At service temperatures in the range of  $800 - 1000^\circ\text{C}$ , CA reacts with  $\text{SO}_3$  from the kiln gases and on cooling (during shutdowns) a further reaction with moisture can occur.

The following reactions have been demonstrated to take place:

♦ In Service



♦ During Shutdowns



As a consequence of all these reactions there occurs

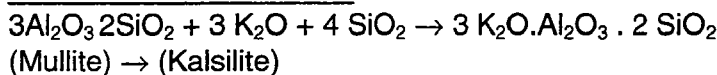
- ♦ a destruction of the bonding and a change of structure
- ♦ a loss of strength

which are claimed as promoting conditions beneficial for the enhanced adhesions of build-ups.

### 1.7.2 Alkali Bursting of Alumina Refractories

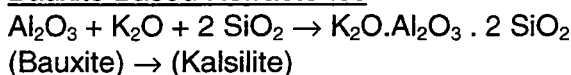
The most well known method by which high alumina bricks are damaged is the so-called alkali-"spalling" or "bursting". By the pick up of alkalis, the formation of feldspathoids takes place which, because of an increase in volume, causes a disruption of the brick at a given depth below the hot face. The ensuing cracking over a large area causes the heads of the brick to spall off. For the various components of high alumina bricks different volume changes occur.

♦ Mullite Based Refractories



$\Delta\text{Volume} = + 29 \%$

♦ Bauxite Based Refractories



$\Delta\text{Volume} = + 2.5 \%$

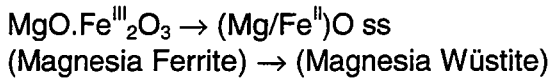
As a consequence, should it be necessary to install high alumina refractories in zones in which the danger of alkali spalling occurs (e.g. transition zone in the vicinity of the kiln type), preference should be given to a bauxite rather than mullite based product.

### 1.7.3 Reducing Atmosphere Attack in Magnesite Refractories

The occurrence of local reducing conditions in the burning and transition zones can, when no protective coating is available, bring about a dramatic loss of brick strength. Damage by this mechanism has been more frequent since the reintroduction of coal firing and has been one of the factors decisive in the necessity to develop new  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  free magnesia refractories i.e. magnesia-spinel products.

Typically, this type of chemical attack takes place on the Fe-containing magnesia ferrite ( $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ ) component, present as a precipitate within the periclase crystals, when the refractories have been in service at approx. 1100°C over an extended period in an oxidizing atmosphere.

Chemically, the following reaction can be considered to occur:



$$\Delta \text{ Volume} = -20 \%$$

The reduction in volume leads to an increase in porosity with a resulting decrease in strength due to the formation of voids.

#### 1.7.4 Gaseous Attack on Dolomite Bricks

Although they give excellent service when protected by a permanent coating, without this protection, the reactive free CaO component of dolomite refractories is very susceptible to reaction by various reagents, all of which result in an increase in volume. Examples of these include:

Reaction	Volume Increase
$\text{CaO} \rightarrow \text{CaS}$	+ 155 %
$\text{CaO} \rightarrow \text{Ca}(\text{OH})_2$	+ 200 %
$\text{CaO} \rightarrow \text{CaCO}_3$	+ 221 %
$\text{CaO} \rightarrow \text{CaSO}_4$	+ 275 %
$\text{CaO} \rightarrow \text{CaCl}_2$	+ 313 %

The MgO component remains in comparison much less reactive to gaseous attack.

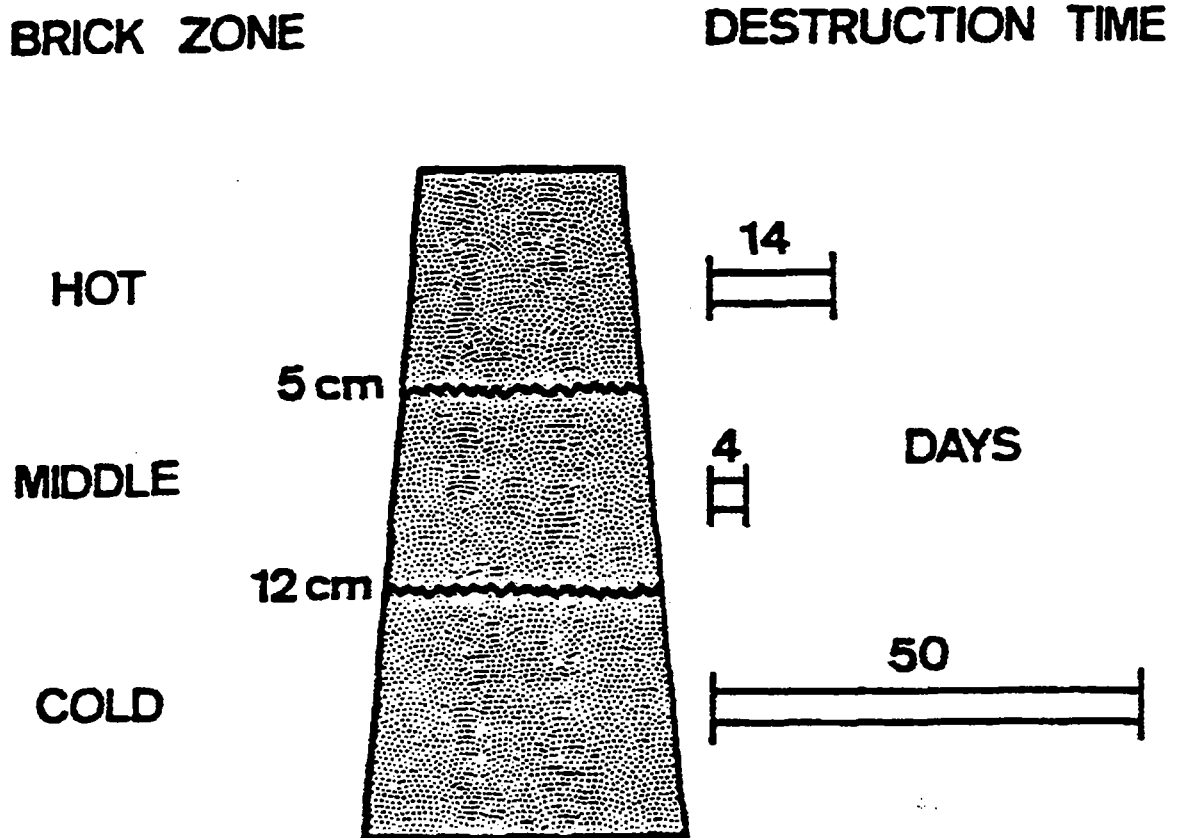
Depending on the temperature conditions and the kiln atmosphere, the following reactions occur in the various sections of a dolomite lining:

- ♦ Middle Brick Zone
  - $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$
  - $\text{CaO} + \text{S}^{-2} \rightarrow \text{CaS}$
  - $2 \text{CaO} + 3 \text{SO}_3 + \text{K}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4$
- ♦ Lower Brick Zone
  - $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$

Because of the increase in volume at a specific temperature and hence depth the increase in volume results first in the formation of cracking and then in the spalling of the hot brick face.

Dolomite bricks are also subject to hydration in air when their temperature is under 450°C. Because used bricks have different concentrations of newly formed minerals, their hydration rate is not the same over the whole structure. It has been shown that the middle CaS containing zones hydrate faster than the hot face, which in turn hydrates faster than the hot face, which in turn hydrates faster than the cold one. This is shown in Fig. 13 showing the rate of destruction of a single used dolomite brick exposed to laboratory air at 22°C and 65% r.h.

Fig. 13 Destruction rates of Dolomite Brick Zones



## **2. COATING: PROPERTIES AND BEHAVIOR**

### **2.1 General**

The formation of durable, protective coating on the refractory lining of a cement kiln is desirable, in a technical as well as in an economical respect, to guarantee steady kiln operations.

Basically, it is known that the properties and behavior of coating have to be regarded as the result of a combination of constructional, process technological and material inherent parameters. The three partial-problems:

- ◆ Formation of coating
- ◆ Adhesion and strength of coating
- ◆ Prevention of ring formation

are closely related to the material parameters as

- ◆ Refractory type
- ◆ Clinker dust and ash characteristics
- ◆ Gas phase and volatile elements

and to the constructional/operational aspects as:

- ◆ Kiln system
- ◆ Kiln operation
- ◆ Operating personnel

### **2.2 Coating**

#### **2.2.1 Definition**

The term "coating" is applied in the cement industry for different phenomena. It is therefore necessary to distinguish between the following:

- ◆ Coating in the cement kiln is the desired protective layer on the refractory lining, which is formed during kiln operation under the influence of high temperature from the traveling material on the refractory lining in the transition and sinter zones.
- ◆ Ring formation is an undesired degree of growth of coating.
- ◆ Incrustations, referred to as build-ups, are "coatings" which are formed below 1100°C by alkali salts and which occur particularly in pre-heater systems.
- ◆ Refractory lining encompasses all construction materials which are intended to eliminate or reduce the effects of thermal strain.

### **2.2.2 Significance of Coating**

Coating has the following functions to fulfill:

- ◆ Protection of the refractory brick against overheating and abrupt temperature changes (improvement of heat distribution).
- ◆ Protection of the refractory lining against the abrasive effect of the moving clinker bed and the dust.
- ◆ Protection of the refractory lining against chemical attack of clinker constituents, fuel ash and gas atmosphere.
- ◆ Augmenting the mixing effect, i.e. improvement of the blending effect of the clinker mass due to unevenness of the coating surface.
- ◆ Reduction of heat radiation and protection of the kiln shell against thermal overloading.

According to experience with large kilns, coating characteristics and behavior were found to be the most significant parameters associated with steady kiln operations. The operating life of refractory linings is substantially longer, when stable coating is achieved over the whole length of the kiln.

Protective coating begins normally in the transition zone which is also the zone, where ring formation may frequently occur.

### **2.2.3 Formation of Coating**

Two basic hypothesis are plausible as to the mechanism of coating formation:

- ◆ Formation of clinker melts (above cat 1280°C) and their sticking together with the refractory lining with simultaneous cementing of solid particles.
- ◆ Adhesion of solid crystalline phases on the refractory lining.

In both cases, chemical and/or physical reactions (impregnation/infiltration) with the upper zone of brick strengthen the adhesion of the coating.

The temperature gradient of coating refractory lining kiln shell effects a further stabilization of the coating as a result of cooling and crystallization. The formation of coating increases to that point at which its inherent insulation characteristics prevent further growth.

### **2.2.4 Thickness of Coating**

Usually, the following classification is applied as to the thickness of coating:

30 - 50 cm	thick coating
~ 20 cm	normal coating
0 - 10 cm	thin coating

Coating thicker than 50 cm is classified as ring formation.

## **2.3 Influencing Parameters**

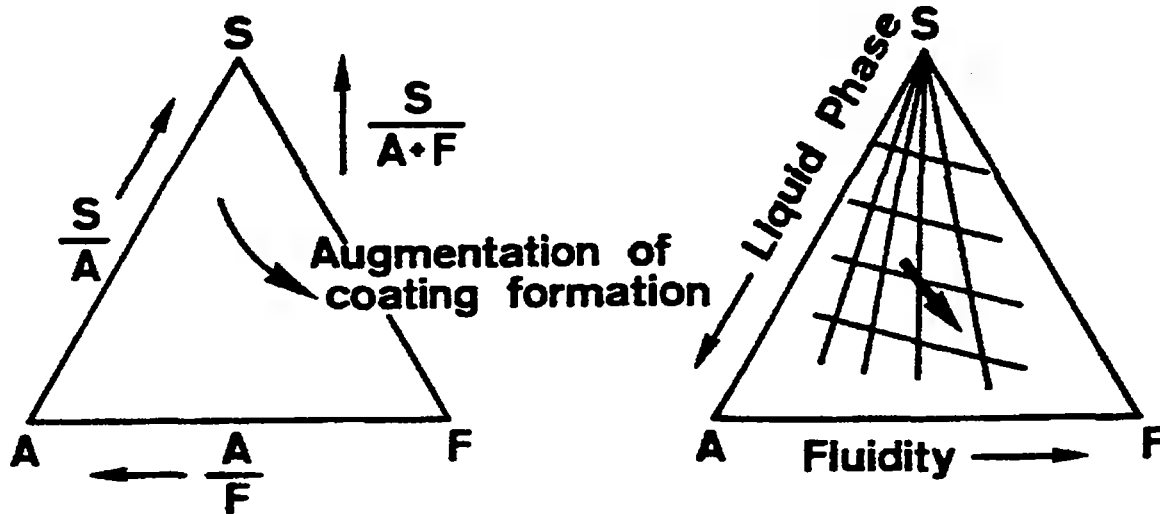
Coating is preponderantly formed from the components of raw material and clinker, whose characteristics and composition primarily determine the quality and quantity of the coating. In addition, the type of fuel and diffusion products of the refractory lining also exert a certain influence.

### **2.3.1 Chemical Composition**

Industrial experience demonstrates that a correlation exists between the characterizing moduli (silica ratio, alumina ratio, lime saturation) and the rate and ability of coating

formation. Within the system  $\text{SiO}_2$   $\text{Al}_2\text{O}_3$   $\text{Fe}_2\text{O}_3$ , i.e. S A F, the dependence of coating formation and chemical composition has been demonstrated as occurring in Fig. 14.

Fig. 14 Correlation of coating formation and chemical parameters



Coating formation is facilitated by decreasing the ratios  $A/F$  and  $S/A$ .

In a second triangle (right) indicating two series of lines, viz. equal percentage of liquid phase at  $1450^\circ\text{C}$  and equal fluidity of the liquid phase it is demonstrated that, disregarding the lime saturation, the tendency to coating formation increases with increasing proportion and fluidity of the liquid phase.

The liquid phase of a clinker is defined as that material present in liquid form, after beginning of the formation of clinker minerals. This usually first forms at temperatures of approximately  $1250^\circ\text{C}$ . This liquid phase content at  $1450^\circ\text{C}$  may be up to 35 %, but on average lies around 25 %.

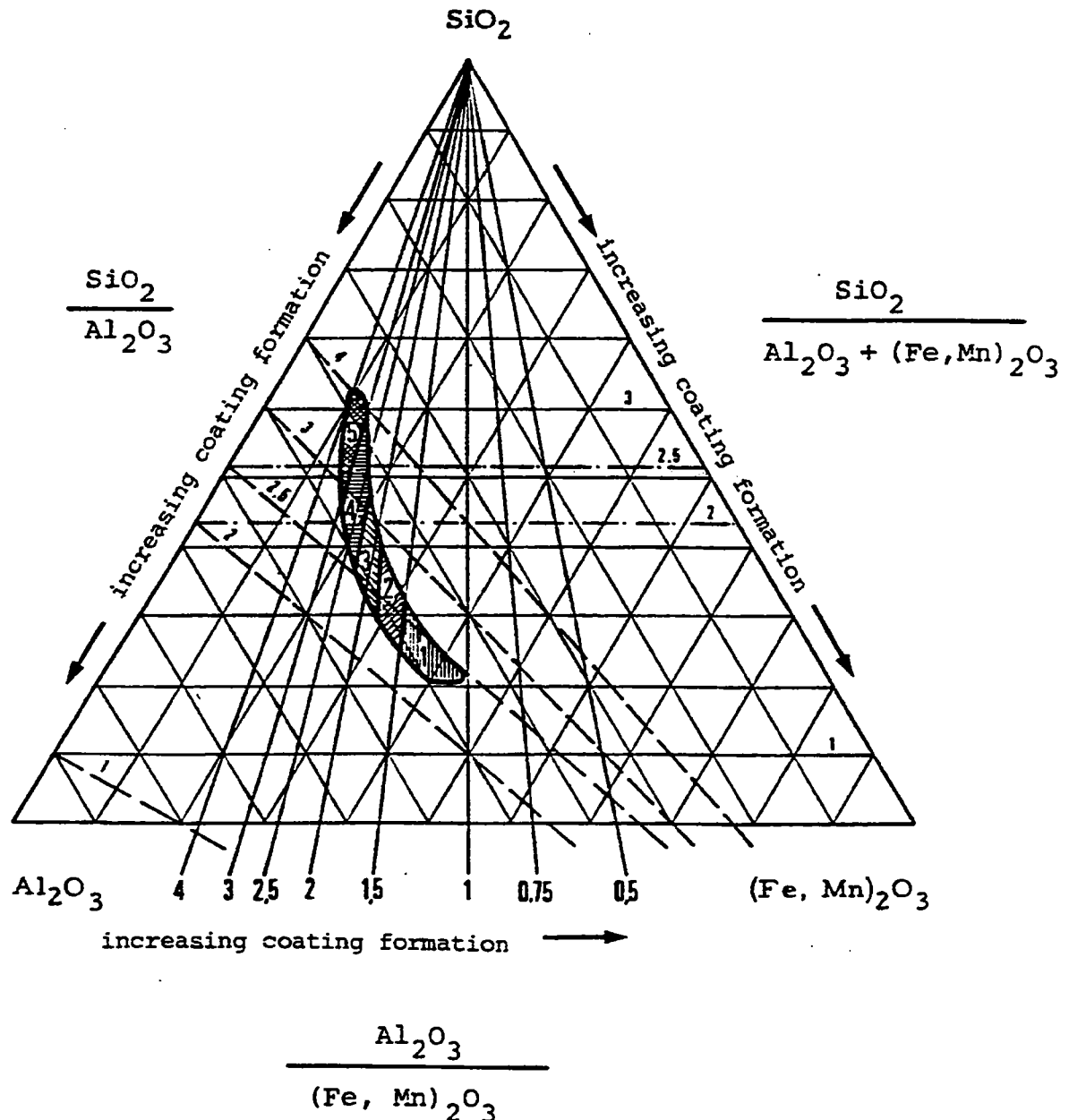
The quantity of liquid phase and its physical properties (viscosity, surface tension, etc.) are dependent on chemical composition and temperature.



From experience, a correlation is known to exist between the quantity of liquid phase ( $C_3A + C_4AF + MgO + K_2O + Na_2O + SO_3$ ) and the thickness of the coating. If a raw mix with less than 20 % potential liquid phase is employed, the formation of coating in the burning zone is expected to be weak, whereas liquid phase contents of more than 25 % lead to thick coating and frequent ring formation.

Another display divides the field of potential coating formation into five areas (Fig. 15).

**Fig. 15** Clinker composition and coating formation as influenced by the ratios of  $SiO_2$   $Al_2O_3$   $(Fe, Mn)_2O_3$



Coating formation is subdivided as follows:

field 1	strong
field 2	medium strong
field 3	medium
field 4	low
field 5	very low

Generally, the following can be deduced from Fig. 14:

- ◆ Increasing alumina ratio and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio impair coating formation and vice-versa.
- ◆ Favorable coating conditions are achieved with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 2.5 to 3.3 and an alumina ratio of 1.8 to 2.3.
- ◆ Favorable coating conditions are achieved at constant medium or high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, by lowering the alumina ratio.
- ◆ Extremely  $\text{SiO}_2/\text{Al}_2\text{O}_3$  high ratios necessitate extremely low alumina ratios.
- ◆ Main influencing parameter is the alumina ratio.

In addition, a number of other measures to improve the tendency to coating formation have been proposed:

- ◆ Lowering of the  $\text{CaCO}_3$  content in the raw mix
- ◆ Addition of  $\text{CaF}_2$  (fluorspar)
- ◆ Addition of pyrites ash

etc.

However, the chemical characteristics of the raw material should not be over-emphasized, since the characteristics of the refractory lining represent additional, determining parameters as to coating formation.

### 2.3.2 Mineralogical Composition

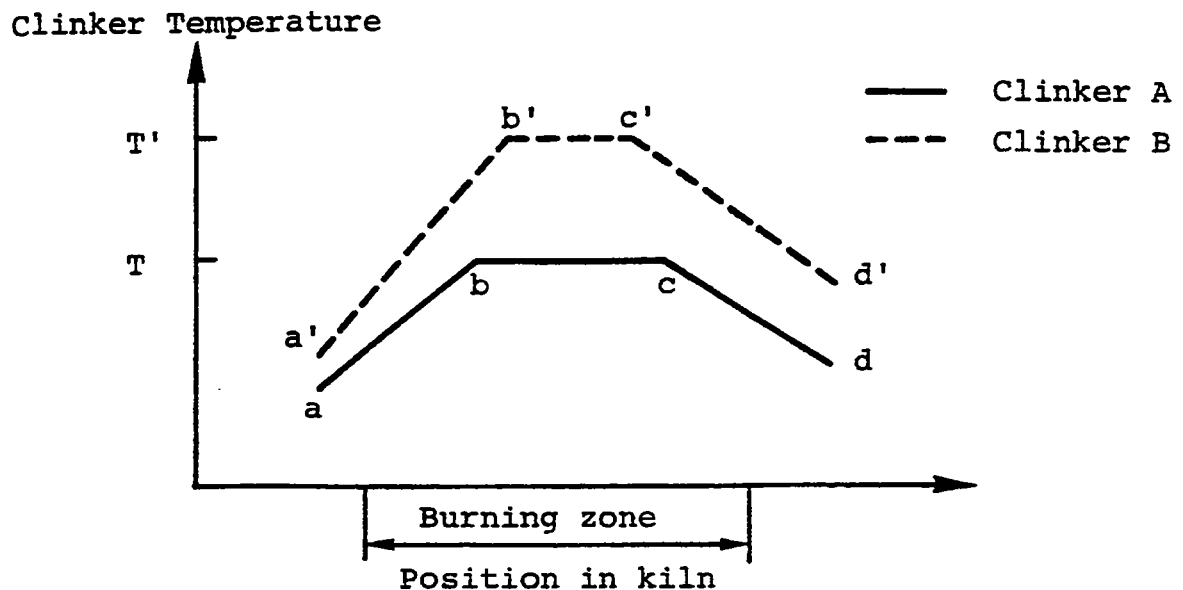
Experience shows that raw mixes containing elevated clay mineral contents and low quartz contents lead to better coating ability than raw mixes of reversed mineralogical composition. Since the mineralogical composition influences the ratios and liquid phase contents, the chemical composition is already a conclusive criterion.

### 2.3.3 Homogeneity of Raw Mix

Inhomogeneity of the raw mix composition is normally responsible for fluctuations in coating formation. This applies not only to chemical inhomogeneity, but also to the variations of the raw mix fineness and to the characteristics of the fuel.

The effects of changes of raw mix properties on the already formed coating layer may be deduced with the aid of Fig. 16.

**Fig. 16 Schematic Temperature profile of kiln clinker as a function of material properties**



Clinker A of good burnability upon up-heating along a - b enters the burning zone at temperature T (point b). It remains during clinker formation at this temperature and then cools down, along the temperature profile c - d. During the contact of clinker A with the refractory lining, a layer of coating is assumed to have been formed.

Any change of the raw mix composition, which impairs its burnability, often leads to a change of clinker melting properties. For the more difficult to burn clinker b let us assume that an increased amount of energy will be necessary resulting in a new temperature profile a' - b' - c' - d'. With this changed profile, the already formed coating layer becomes softer, more fluid, and is easily scraped off by clinker B. If the refractory linings are already worn out, the kiln shell will become hotter and perhaps even red spots may occur. In any case, the refractory lining in the burning zone will be weakened as a result of the new temperature at the brick surface. Frequent changes and loss of coating (due to fluctuation of composition of raw mix) particularly in big kilns often results in a considerable decrease in refractory life caused by spelling.

#### 2.3.4 Circulating Elements

Circulating elements are the alkalis ( $K_2O$ ,  $Na_2O$ ), chlorine ( $Cl$ ) and sulfur ( $SO_2$ ,  $SO_3$ , eventually  $S^{2-}$ ). They evaporate from the raw materials (raw mix and fuel) and condense on the colder raw mix and penetrate into the refractory lining. They play a significant role with regard to the stability of coating and refractory lining life, but influence coating formation to a lesser extent.

Alumina-rich refractory bricks are easily infiltrated by alkalis which react with the brick constituents forming minerals in this zone, such as leucite and kalsilite. These minerals crystallize upon cooling and lead to spalling of the brick surface. Such reactions don't occur between the alkalis and the basic bricks. Corrosion of bricks is also observed, if sulfates are present in notable amounts. The destructiveness of alkali sulfates (and chlorides) on coating is caused by the following mechanism:

- ◆ The sulfate-melt penetrates and becomes enriched in the pores and cracks of the brick, the position of enrichment depending upon the thermal gradient.
- ◆ Periodic changes of the temperature gradient produce both melting and recrystallization, which results in crack formation vertical to the temperature gradient, due to pressure of crystallization.

Such an infiltrated zone is the cause for the spalling of 4 - 6 cm thick layers of brick and adhering coating. As a rule of thumb it can be said that large quantities of alkali and sulfate are always especially harmful, if a molar excess of sulfate exists.

### 2.3.5 Crystal phases

As already discussed, coating formation is mainly considered as being controlled by the properties of the clinker liquid phase.

However, there is also another possibility to be considered: the compaction of powdery materials at high temperatures by sintering or recrystallization. This effect may be explained by the preferential grow of bigger crystals at the expense of smaller ones, a diffusion process which takes place at temperatures below the melting points of the substances.

In nearly all cases in laboratory tests as well as under plant conditions a small layer of  $C_2S$ , less than 1/2 mm in thickness can be found in the contact zone between brick surface and coating, whereby the crystals of  $C_2S$  in this zone seem to be glued together without interstitial phases. The  $C_2S$  zone extends into coating as well as into the upper parts of the (porous) brick to about 1 mm in depth, thus connecting both, brick and coating.

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**Wed 1<sup>st</sup> March 2000**

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I look forward to hearing from you and to co-operating with you in future in the supply of your requirements

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